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Permeation of Oxygen and Moisture Through Vacuum Web Coated Films

U. Moosheimer and H.-C. Langowski, Fraunhofer Institute for
Process Engineering and Packaging, Germany

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ABSTRACT

Worldwide 15,000 km² of polymer films are vacuum web coated with inorganic layers per year. Two third of these coatings are used by the packaging industry. Coatings drastically improve the barrier of polymers against the permeation of gases, moisture and flavor. For final packaging applications, coated layers are normally protected by laminating to another film.

On laboratory as wells as industrial scale, the influence of various production parameters on the permeation through coated barrier films and final high barrier laminates was studied by using different

- types of substrate films,
- kinds of pretreatment,
- inorganic coatings materials and
- lamination adhesives.

The different substrate films, as biaxially oriented polypropylene (BOPP), polyethylene-terephthalate (PET) and ethylene-tetrafluoroethylene-copolymer (ETFE), were either pretreated at the film production site by a standard Corona atmospheric plasma or in-situ before the vacuum web coating by an oxygen low pressure plasma.

These films were vacuum web coated with aluminum (Al), aluminum oxide (AlO_x) or silicon oxide (SiO_x) and laminated against BOPP or polyethylene (PE) films using polyurethane and ORMOCER® adhesives.

Finally, different mechanisms for the permeation of oxygen and moisture through films with an inorganic barrier layer could be identified. Thereby, the barrier layer itself as well as substrate surface and adhesive layers adjacent to it determine the permeability through the final laminate.

INTRODUCTION

In food and pharmaceutical applications, film laminates are requested that possess high barriers for gases, water vapor and flavors. Low cost barrier films can be produced by vacuum web coating with inorganic barrier layers.

THEORETICAL BACKGROUND OF PERMEATION

Through Polymer Films

The permeation mechanism of gases, water vapor and flavor through polymer films depends on

- how many molecules can be dissolved in the polymer, e.g. the **solubility** coefficient *S* of the permeating substance in the polymer and
- how fast the molecules can move inside the polymer, e.g. the **diffusion** coefficient *D*.

The permeability *P* is given by

$$P = D \times S$$

Laminating different polymer films together, the total permeability (*P*_{total}) can be calculated from the permeabilities (*P*₁, *P*₂, ...) of the components by the simple equation, also used for conductivity in series as the electrical analogous:

$$P_{\text{total}}^{-1} = P_1^{-1} + P_2^{-1} + \dots$$

The driving force is the difference in concentration between both sides of the polymer film. The different substances permeate homogenously through the laminates, as schematic shown in Figure 1.

Through Inorganic Barrier Layers

The permeation through vacuum coated inorganic barrier layers, as Al, AlO_x and SiO_x, predominantly occurs at macroscopic defects of inorganic layers. There is practically no permeation through the bulk material of the layers. In contrast to pure polymer laminates, the defects in the inorganic barrier layers are the bottleneck for permeating substances, as demonstrated in Figure 2. As a consequence, the permeability through the polymer close to the defects influences the total permeability much stronger than at the outsides of the laminate.

Due to the sideways diffusion to and from the bottlenecks (macroscopic defects), many small holes in a barrier layer are much more effective in compromising the systems barrier properties than a few large holes with the same total area [1]. This is

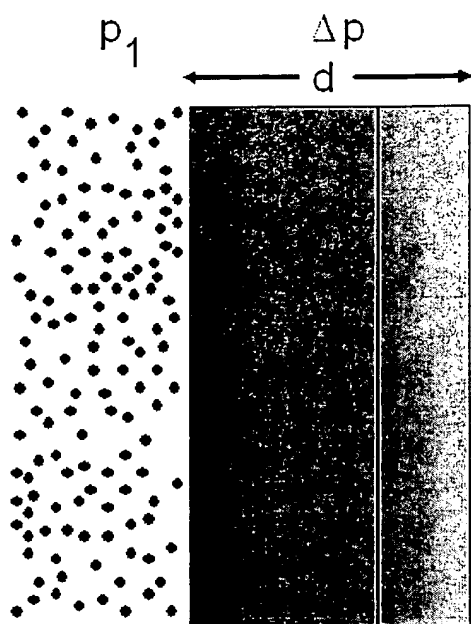


Figure 1. Permeation mechanism (schematic) through a laminate containing two homogenous polymers

theoretically approved for the case of a concentration independent diffusion coefficient, as for O_2 , N_2 and CO_2 , but not for H_2O and flavor substances.

Concluding, the total permeability mainly depends on the size as well as the density of the defects and the permeability through the polymers next to the inorganic barrier layer.

To get high barrier laminates by use of this synergy effect, there must be

- a low density of defects in the barrier layer and
- a polymer possessing a high barrier next to the inorganic vacuum coated layer.

EXPERIMENTAL SETUP

In an industrial round robin test, different BOPP films were vacuum web coated with Al and laminated with a two component polyurethane adhesive by a converter [2].

Parallel, in laboratory scale BOPP films were low pressure oxygen plasma pretreated and quasi in-situ coated with Al, AlO_x or SiO_x in a roll-to-roll coater [3]. The coated films were laminated against standard BOPP copolymer films.

The topography of the film surfaces was analyzed by Atomic Force Microscopy (AFM) [4].

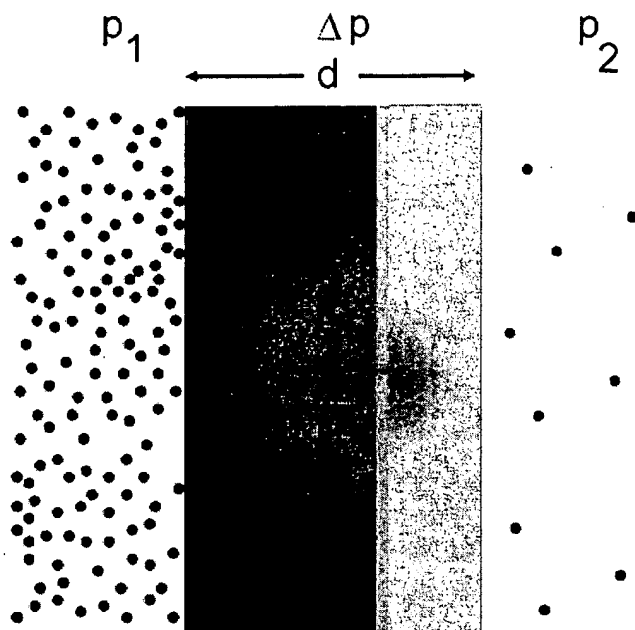


Figure 2. Permeation mechanism (schematic) through a three layer laminate containing an inorganic barrier layer

According to DIN 53380, part 3 the oxygen permeability was measured at 23 °C and 50 % relative humidity (unless mentioned otherwise) by an electrochemical sensor. The moisture permeability was determined at 23 °C and 85 to 0 relative humidity according to DIN 53122, part 1.

EXPERIMENTAL RESULTS

Thickness of the Barrier Layer

Using laminates with vacuum web coated barrier layers, the most important coating parameter consists in the thickness of the coated layers. As to be seen in Figure 3, the first 10 nm of Al coating reduce the O_2 permeability of a 12 μm thick PET film by a factor of 2. At an Al thickness of more than 60 nm the O_2 barrier is improved only slightly by thickness.

From an industrial point of view, the layer thickness must be optimized on the one hand for low coating costs and on the other side for high barrier values. Typical values are between 40 and 60 nm.

From a scientific point of view, the surface of a PET film possesses a microscopic roughness, as to be seen in Figure 4 and Figure 5. Hence an Al coating of 10 nm being only a few nanometers thicker than the total roughness cannot closely cover the whole film surface. There are still non-coated peaks and voids, but the coating already reduces the O_2 permeability by a factor 2. Thicker layers than 60 nm only slightly improve the O_2 permeability. This behavior is symptomatic for permeation being based on macroscopic defects in the barrier layer

[1]. These transmission gates for gas, water vapor and flavor are usually generated by contaminating particles or antiblock agents, as to be seen in Figure 6. Other defects are caused the handling of the coated films. Scratches caused by the direct contact of barrier layers to winding rolls of vacuum coaters, cutting and lamination machines destroy the barrier properties. Mechanical loads can also reduce the barrier. For example, the damaging of the O_2 barrier of inorganic barrier laminates starts at linear elongation of 2 to 3 % depending on the inorganic material [2]. Contrary to the option of most people, SiO_x coatings are as stress resistant as Al coatings.

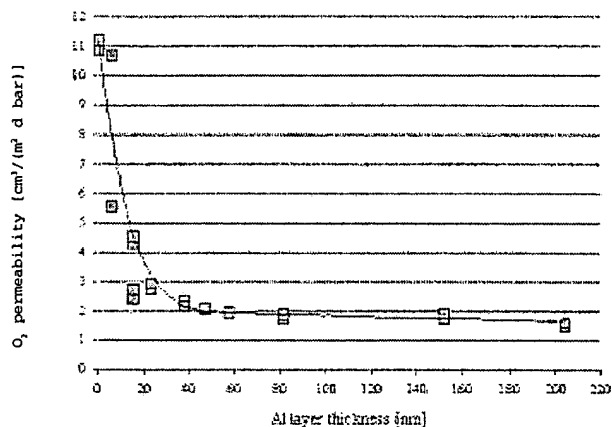


Figure 3. O_2 permeability through PET films coated with different thick Al layers (measured at 23°C and 75% relative humidity) [5]

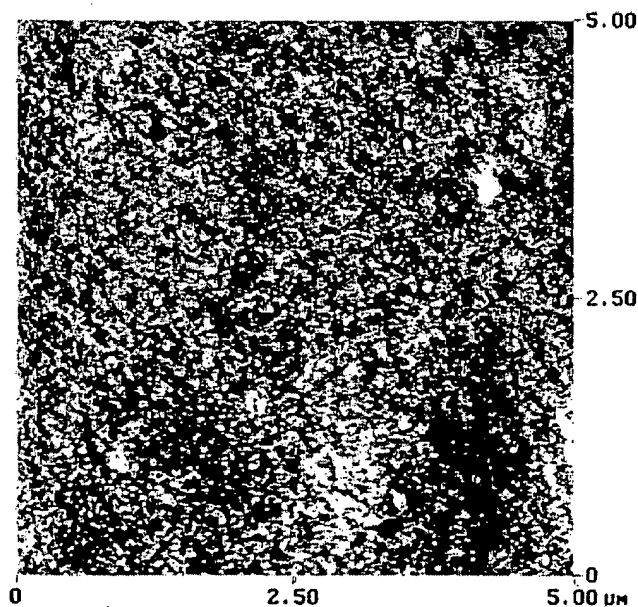


Figure 4. Surface structure of a PET film analyzed by AFM (atomic force microscopy) [6]

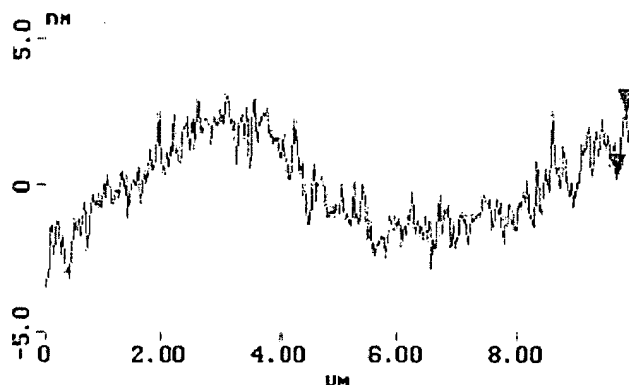


Figure 5. Surface roughness profile of a PET film analyzed by AFM (atomic force microscopy) [6]

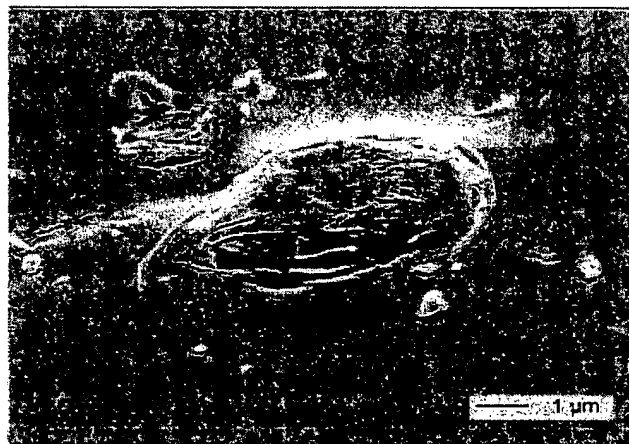


Figure 6. Antiblock particle in a coated PET film analyzed by high resolution SEM (scanning electron microscopy) [7]

Thickness of the Polymer Films

How the thicknesses of the substrate film and of the film that is laminated on top of the barrier layer influence the final barrier properties? To obtain an idea, permeating molecules may be regarded as cars in a heavy traffic jam that is caused by a bottleneck (the defect in the barrier layer). If we put a certain number of cars on the road far away from the bottleneck, their movement (through the substrate film) is fast until they reach the end of the traffic jam. After leaving the jam, their movement (through the laminated film) is again fast. If the bottleneck (the defect) is narrow enough, it does not matter if we make the road distance (the film thickness) before and after the bottleneck shorter or longer, as most of the time is lost in the traffic jam. Hence, replacing a 30 μm thick BOPP substrate film by a 7 μm thick film with the same surface properties does not reduce the barrier properties of the final vacuum coated laminate [8].

To illustrate the influence of the substrate film thickness, the O_2 permeability calculated according to [1] for different thick

PET films is plotted in Figure 7. The permeability can be calculated in the limits:

- film thickness much smaller than defect size (left branch of the curve) and
- film thickness much bigger than defect size (right branch of the curve).

It was assumed, that there are 8000 cylindrical defects per square centimeter with a diameter of $1\text{ }\mu\text{m}$ [1]. Due to the hyperbolic decline of the O_2 permeability with film thickness, only the PET film next to the barrier layer influences the total O_2 permeability. The relevant thickness is below the defect size of $1\text{ }\mu\text{m}$. The combination of the film in its relevant thickness with the layer defects represents the bottleneck for permeating molecules. Hence smaller defects will again reduce the relevant thickness of the permeation determining material.

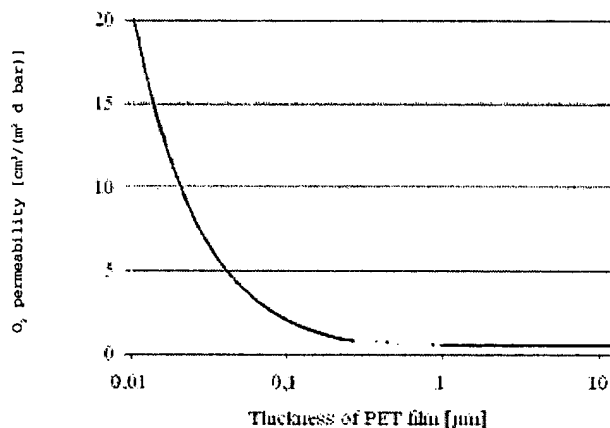


Figure 7. Calculation of the O_2 permeability at an inorganic barrier layer for different thick PET films

Smoothing of the Substrate Film

The number of defects can be reduced by using smooth polymer films. For example, polymer films can be smoothed by low pressure vacuum pretreatment of the substrate polymer, as to be seen in Figure 8. Because the pretreatment only influences the O_2 permeability but not the adhesion, the improvement of the barrier results from the smoothing of the surface [2].

Pre-Coated and Co-extruded Substrate Films

In order to obtain the synergy effect for vacuum web coating, e.g. inorganic barrier layer plus barrier polymer next to the coated layer, options are to use a coextruded film, a pre-coated substrate film or a barrier adhesive. Due to its low penetration depth of a few 10 nanometer, Corona pretreatment is not sufficient to setup an organic barrier layer on the substrate film, as a thickness of some $0.1\text{ }\mu\text{m}$ is requested for organic barrier layers. For example, film producers coat inline BOPP films

with acrylates or co-extrude PEN/PET on PET films. As to be seen in Figure 9., the acrylate pre-coating reduces the O_2 permeability through the BOPP film for all three inorganic barrier layers by one order of magnitude. Similarly, after vacuum web coating, the water vapor permeability through co-extruded $12\text{ }\mu\text{m}$ PEN/PET films is one magnitude lower than through standard $12\text{ }\mu\text{m}$ PET films, as to be seen in Figure 10. [9].

Barrier Adhesives

Normally, inorganic barrier layers of vacuum web coated polymer films are laminated against other polymer films, in order to avoid destruction of the sensitive barrier layers. There the adhesive is next to the barrier layer. Using high barrier adhesives, as ORMOCER®, allows to use again the synergy between the inorganic barrier layer and the adhesive, as to be seen in Figure 11.

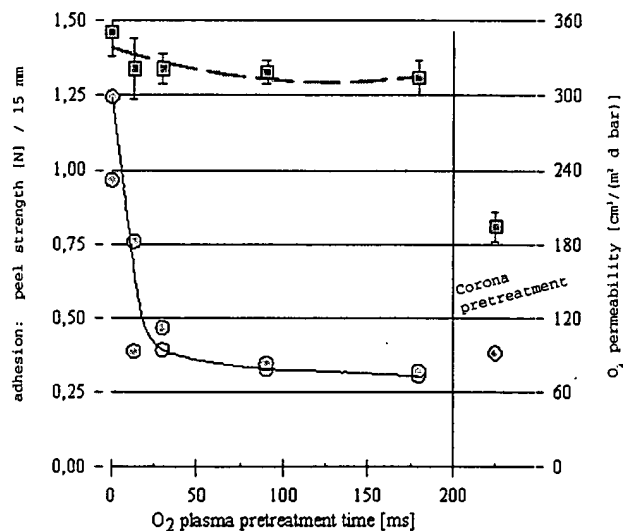


Figure 8. Adhesion (squares) and O_2 permeability (dots) through O_2 low pressure plasma pretreated AlO_x coated BOPP homopolymer films [2]

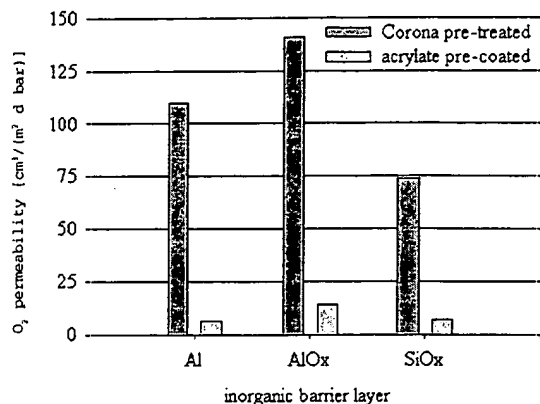


Figure 9. O₂ permeability through Corona pretreatment or acrylate pre-coated BOPP films [8]

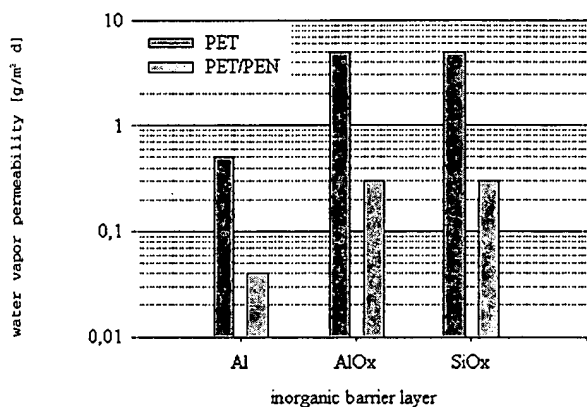


Figure 10. Water vapor permeability through PET and PEN/PET co-extruded films [9]

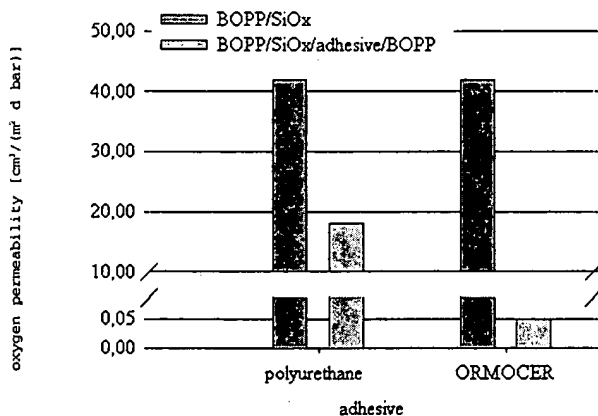


Figure 11. O₂ permeability through SiO_x created BOPP films laminated to BOPP films by different adhesives [11]

Differences in Permeation of Water Vapor and Oxygen through Inorganic Barrier Layers

Different industrial Al coated BOPP films were laminated against a 17 μm thick BOPP copolymer film using polyurethane adhesive. The laminates possess different oxygen and moisture permeabilities. But, as shown in Figure 12, the laminate with the lowest O₂ permeability has the highest moisture permeability and vice versa. The three BOPP films differ in their surface properties. The different surface topographies can be seen even after coating by AFM analysis, as to be seen in Figure 13 and Figure 14. Hence the various structures of the inorganic barrier layers yield different macroscopic defects. As an additional effect, due to its polar structure, acrylate pre-coating reduces the permeability for non-polar O₂ molecules stronger than for polar water molecules.

In another experiment, on laboratory scale 12 μm thick PET films were coated with Al₂O₃ or SiO_x in different thicknesses, obtained by variation of the web speed [10].

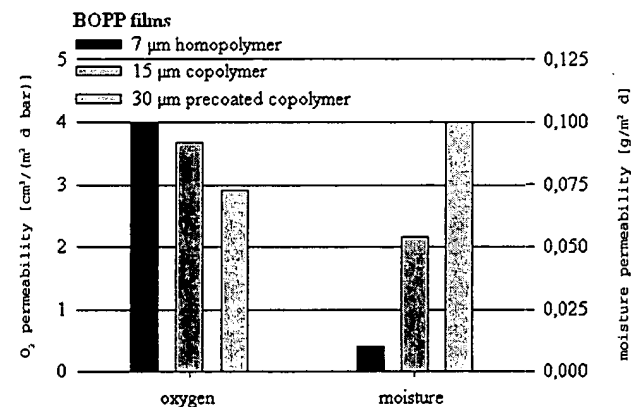


Figure 12. Different thick BOPP films: Influence on oxygen and moisture permeability of Al coated barrier laminates [2]

The thinnest Al₂O₃ layers of 15 nm were obtained at the highest web speed of 7 m/min, the thickest layers of 100 nm at a speed of 1 m/min. As to be seen in Figure 15, the highest oxygen but lowest moisture permeabilities are obtained by low web speeds, i.e. on thick Al₂O₃ layers. Hence, there are different mechanism for the oxygen and moisture permeation, see also Figure 12.

Similarly, 420 nm (1 m/min) thick SiO_x coatings on ETFE films show a higher moisture barrier, e.g. lower moisture permeability, than 60 nm (7 m/min) thin layers as to be seen in Figure 16.

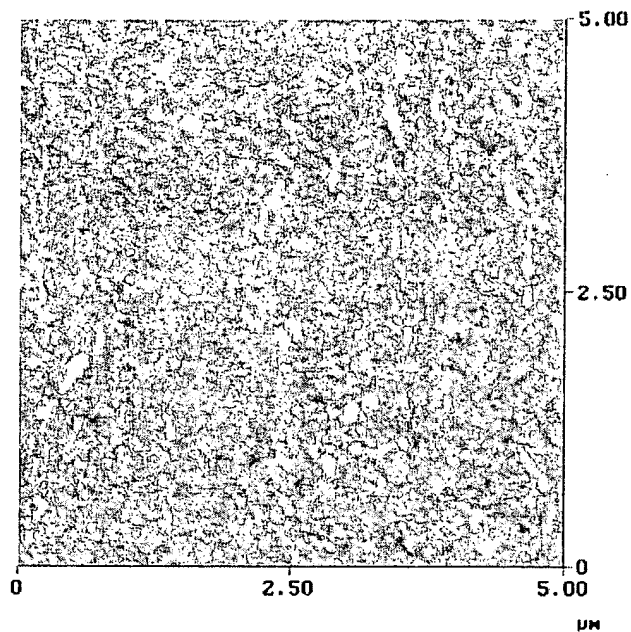


Figure 13. Surface structure of an Al coated BOPP homopolymer films analyzed by AFM (atomic force microscopy) [2]

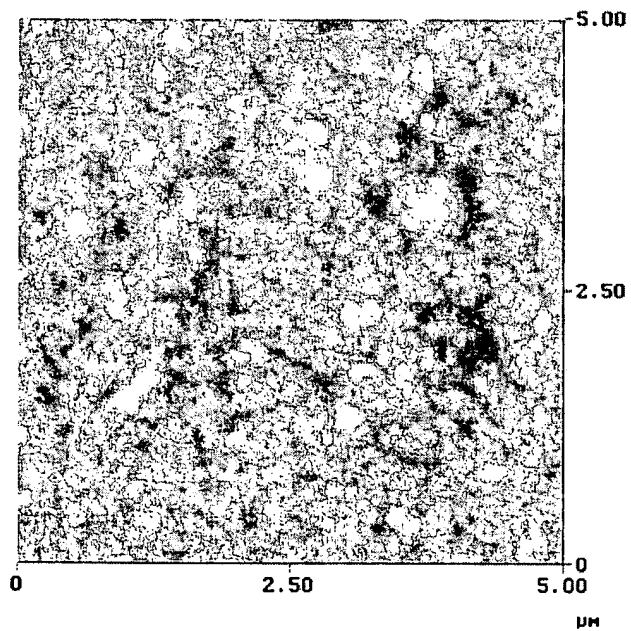


Figure 14. Surface structure of an Al coated BOPP copolymer film analyzed by AFM (atomic force microscopy) [2]

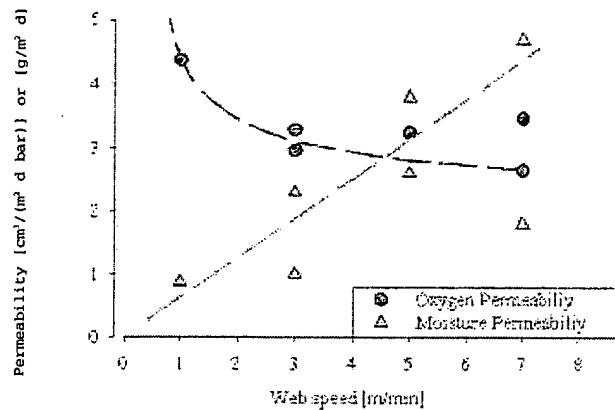


Figure 15. Moisture permeability of Al_2O_3 coated PET ($12\mu\text{m}$) films

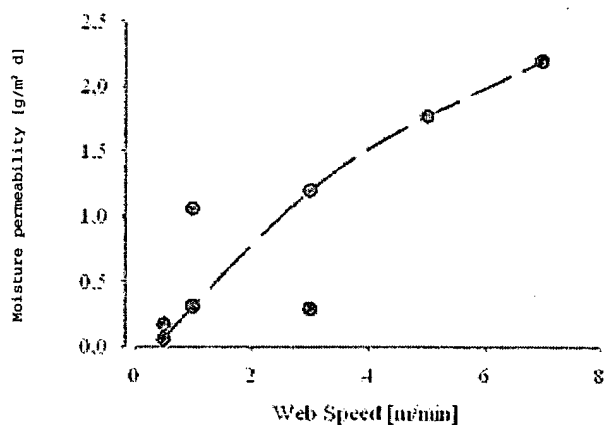


Figure 16. Moisture permeability of SiO_x coated ETFE ($20\mu\text{m}$) films at different web speeds

CONCLUSION

The permeation through vacuum web coated laminates containing an inorganic barrier layer is determined by

- the density and type of macroscopic defects in the barrier layer and
- the polymer material at the defects.

The barrier of the final laminate can be improved by reducing the defects. Successful options are thick coating and coating smooth or plasma smoothed substrate films.

Thin high barrier polymer layers at the barrier layer drastically raise the barrier. On the substrate side pre-coating or co-extruding can be used and on the other side barrier adhesives.

Finally the structures of barrier layers and polymer films influence the oxygen and moisture permeability in a different way. Modifying the structure of the inorganic layer by changing the properties of the substrate film and selecting the type right type of films may allow to produce selective barrier against oxygen but not water and vice versa.

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REFERENCES

1. A.S. da Silva Sobrinho, M. Latrèche, G. Czeremuszkin, J. E. Klemberg-Saphieha, M. R. Wertheimer, "Transparent Barrier Coatings on Polyethylene Terephthalate by Single- and Dual-frequency Plasma-Enhanced Chemical Vapor Deposition," *J. Vac. Sci. Technol. A*, 1 (1998) and references therein
2. Ch. Bichler, K. Mayer, H.-C. Langowski and U. Moosheimer, "Influence of Polymer Film Surfaces on Adhesion and Permeation Properties of Vacuum Web Coated High Barrier Films and Laminates: Results of a Cooperative Research Project," *Proc. of the 41st Annual Technical Conference*, Boston, 1998. Society of Vacuum Coaters, Albuquerque, p. 349, 1998
3. C. Bichler, M. Bischoff, H.-C. Langowski, U. Moosheimer, "Transparent Barrier Coatings for Flexible Packagings: Industrial and Research Activities in Germany," p. 378, *Proc 39th Ann Tech Conf of SVC*, Philadelphia, 1996
4. U. Moosheimer, „Plasmavorbehandlung und Beschichtung von Kunststoffolien; Teil 1: Beschichtung von unbehandelten Kunststoffolien," *Mat.-wiss. u. Werkstofftech.*, 29, 312 (1998)
5. H. Utz, *Barriereigenschaften aluminiumbedampfter Kunststoffolien* Doctoral Thesis, Universität München, 1995
6. Fraunhofer-Institute for Process Engineering and Packaging, Freising, 1998, internal measurements
7. H.-C., Langowski, „Barriereigenschaften von beschichteten Packstoffen: Eine Übersicht," *Allgemeine Papier-Rundschau*. 5, 107 - 113 (1996)
8. U. Moosheimer, „Plasmavorbehandlung und Beschichtung von Kunststoffolien; Teil 2: Experimentelle Ergebnisse der Plasmavorbehandlung von Kunststoffolien," *Mat.-wiss. u. Werkstofftech.*, 29, 345 (1998)
9. R. Davis and H. Peiffer, „Vorteile koextrudierter PET-Folien für die flexible Verpackung," *Proc. of the Symp. at the FachPack*, Nürnberg 1998, Fraunhofer-Institute for Process Engineering and Packaging, Freising, 1998
10. U. Moosheimer, H.-C. Langowski and Ch. Bichler, "New Cost Efficient Components for the Encapsulation of Photo-Voltaic Modules," *Proc. of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, 6-10 July 1998, Vienna
11. M. Gessler, H. Bader, M. Hoffmann and S. Amberg-Schwab, „Transparente, flexible Hochbarrierefolien durch Kombination von aufgedampften anorganischen Schichten mit anorganisch-organischen Hybridpolymeren," *Coating* 10, 358 (1997)